

QUINOXALINE-CONTAINING AB₂ MONOMER FOR HYPERBRANCHED AROMATIC
POLY(ETHER-KETONES)

CROSS REFERENCE TO RELATED APPLICATION

5 This application claims priority of the filing date of Provisional Application serial number 60/453,333, filed 02-28-2003.

RIGHTS OF THE GOVERNMENT

The invention described herein may be manufactured and used by or for the Government of the United States for all governmental purposes without the payment of 10 any royalty.

BACKGROUND OF THE INVENTION

The present invention relates to a new quinoxaline-containing AB₂ monomer that is useful for the preparation of hyperbranched poly(ether-ketones).

Dendritic macromolecules such as dendrimers and hyperbranched polymers are 15 a new class of highly branched polymers that have distinctly different properties from their linear analogs. Both dendrimers and hyperbranched polymers have much lower solution and melt viscosities than their linear analogs of similar molecular weights. They also have a large number of chain-ends whose collective influence dictates their overall physical and/or chemical behaviors. These features are attractive in terms of 20 processability and offering flexibility in engineering required properties for specific applications. However, there is a practical advantage that hyperbranched polymers have over dendrimers at "raw material" level. Although dendrimers have precisely controlled structures (designated as generations), their preparations generally involve tedious, multi-step sequences that are impractical and costly in scale-up production. 25 Synthesis of a hyperbranched polymer, on the other hand, is a one-pot process. Large

quantities of hyperbranched polymers can be easily produced from AB_x ($x \geq 2$) monomers.

Because of their excellent thermal and mechanical properties, as well as their optical and electronic characteristics, aromatic, fused heterocyclic polymers such as 5 polyquinoxalines and polybenzoxazoles continue to attract considerable attention. However, they have limited processability due to the nature of fused ring systems. Their insolubility and their softening temperatures are generally above their degradation 10 temperatures. Chemical modification on the these materials, for example, by the use of solubilizing pendants or flexible units in the main chain, has been successful to improve their processability, allowing the optimization of their properties as a function of 15 processability. Another viable approach to achieving this objective is to incorporate the elements of local rigidity and global randomness into the macromolecular architecture. Local rigidity provides the thermal, electronic and optical characteristics of the aromatic fused systems while global randomness frustrates entanglement of the polymer chains, leading to greater solubility. Dendritic structures clearly embody these qualities. 20 However, as noted previously, hyperbranched structures have greater synthetic practicality.

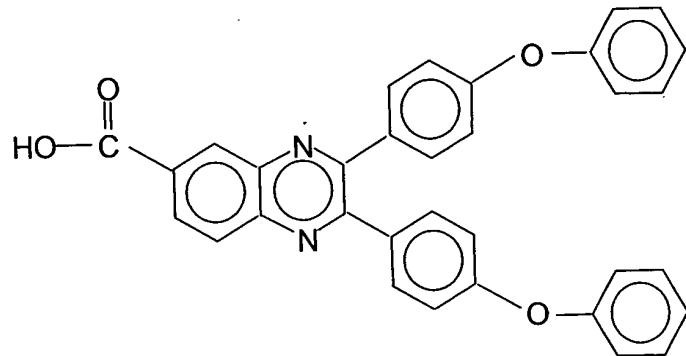
Accordingly, it is an object of the present invention to provide a novel quinoxaline-containing AB_2 monomer that is useful for the preparation of hyperbranched 20 poly(ether-ketones).

Other objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may

be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

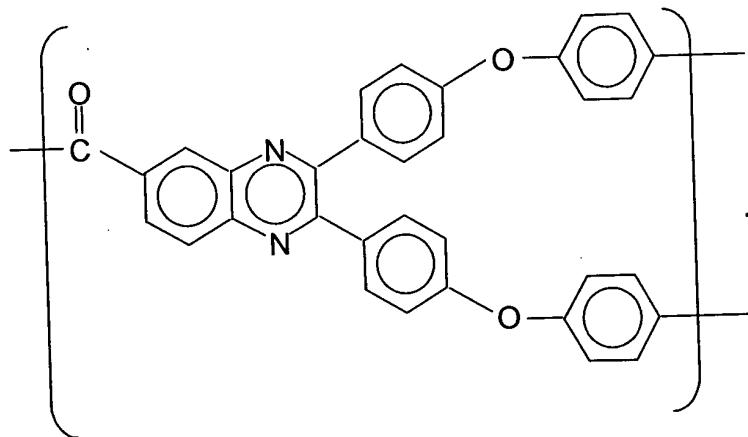
SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a novel AB₂ monomer,
 5 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, having the formula:



The AB₂ monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, is synthesized as set forth in the examples which follow.

The AB₂ monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, is
 10 useful for preparing the hyperbranched ether-ketone polymer:



The following examples illustrate the invention:

Example 1

1-(2-Methyl-3-butyn-2-ol)-2-(4-phenoxyphenyl)ethyne

Into a 1 L three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, 4-bromodiphenylether (50.1g, 201 mmol), freshly distilled 2-methyl-3-butyn-2-ol (64.3g, 892 mmol), copper(I) iodide (0.11g, 0.60 mmol), triphenylphosphine (0.33g, 1.3 mmol), and bis(triphenylphosphine)palladium(II) chloride (1.12g, 1.6 mmol) were placed. The solids were carefully washed in with triethylamine (500 mL). The mixture was heated under reflux for 24h. After the reaction mixture had been allowed to cool to room temperature, the solution was filtered through silica gel. The filtrate was poured into 5% hydrochloric acid solution and diluted with methylene chloride. After separation from the aqueous phase, the organic phase was subjected to purification via a silica-gel column chromatography with methylene chloride/hexane elution to give 40.5g (80% yield) of light yellow oil. Anal. Calcd. for C₁₇H₁₆O₂: C, 80.93%; H, 6.39%; O, 12.68%. Found: C, 80.88%; H, 6.43%; O, 12.89%. Mass spectrum (m/e): 252 (M⁺, 100% relative abundance).

Example 2

(4-Phenoxyphenyl)ethyne

Into a 1 L three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, 1-(2-methyl-3-butyn-2-ol)-2-(4-phenoxyphenyl)ethyne (40.0g, 159 mmol) was dissolved in toluene (700 mL). A solution of potassium hydroxide (2.2g, 39.2 mmol) in methanol (40 mL) was added. The mixture was heated under reflux 14h. The solution was concentrated to approximately 100 mL and then

purified by silica-gel column chromatography with pentane elution to give 28.0g (90% yield) of light yellow oil. Anal. Calcd. for C₁₄H₁₀O: C, 86.57%; H, 5.19%; O, 8.24%. Found: C, 86.52%; H, 5.25%; O, 8.29%. Mass spectrum (m/e): 194 (M⁺, 100% relative abundance).

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Example 3

1,2-Bis(4-phenyloxyphenyl)ethyne

Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, (4-phenyloxyphenyl)ethyne (28.0g, 144 mmol), 4-bromodiphenylether (27.7g, 151 mmol), copper(I) iodide (0.10g, 0.53 mmol), triphenylphosphine (0.30g, 1.1 mmol), and bis(triphenylphosphine)palladium(II) chloride (1.00g, 1.4 mmol) were placed. The solids were carefully washed in with triethylamine (500 mL). The mixture was then heated under reflux for 24h. After the reaction mixture had been allowed to cool to room temperature, the solution was filtered through silica gel. The filtrate was poured into 5% hydrochloric acid solution and diluted with methylene chloride. After separation from the aqueous phase, the organic phase was subjected to a silica-gel column chromatography with petroleum ether elution to remove the excess 4-bromodiphenylether and then methylene chloride/hexane (33/67, v/v) elution to give 42.3g (81% yield) of white crystals. It was again recrystallized from toluene to give 32.1g (62% yield) of white flakes, m.p.173-174°C. Anal. Calcd. for C₂₆H₁₈O₂: C, 86.17%; H, 5.01%; O, 8.83%. Found: C, 86.13%; H, 5.40%; O, 8.43%. FT-IR (KBr, cm⁻¹): 738, 3039, 3061. Mass spectrum (m/e): 362 (M⁺, 100% relative abundance). ¹H NMR (DMSO-d₆, ppm) δ 6.97-7.00 (dd, 4H, Ar), 7.04-7.08 (m, 4H, Ar), 7.15-7.21 (t, 2H, Ar), 7.38-7.44 (t, 4H, Ar), 7.49-7.52(d, 4H, Ar).

Example 4

1,2-Bis(4-phenyloxyphenyl)benzil

(Method 1) Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, a dropping funnel and a nitrogen inlet, 1,2-bis(4-phenyloxyphenyl)ethyne (4.0g, 11.0 mmol) and methyltrialkyl ammonium chlorides (Adogen 454, 1.25g) were dissolved in methylene chloride (200 mL). A solution of potassium permanganate (16.0g, 101 mmol) in acetic acid (30 mL) and water (500 mL) was slowly added through a dropping funnel. The mixture was gently heated under reflux for 10h. After cooling down to room temperature, the mixture was poured in large flask, potassium bisulfate was added until the mixture became clear, and then a small amount of sodium bicarbonate was added. The organic layer was then separated, dried over magnesium sulfate, filtered, and solvent was removed under the reduced pressure to give 4.22g of light yellow solid, which was re-dissolved in hot ethanol or heptane and allowed to cool to room temperature to give 3.88g (89% yield) of light yellow powder, m.p.119-120°C. Anal. Calcd. for C₂₆H₁₈O₄: C, 79.17%; H, 4.60%. Found: C, 79.83%; H, 4.89%. FT-IR (KBr, cm⁻¹): 1667. Mass spectrum (m/e): 394 (M⁺, 100% relative abundance). ¹H NMR (DMSO-d₆, ppm) δ 7.00 -7.06 (dd, 4H, Ar), 7.06-7.11 (m, 4H, Ar), 7.20-7.25 (t, 2H, Ar), 7.37-7.44 (t, 4H, Ar), 7.78-7.96(dd, 4H, Ar). ¹³C NMR (DMSO-d₆, ppm) δ 117.44, 120.46, 125.06, 127.51, 130.16, 132.20, 154.84, 155.89, 162.35, 163.56.

(Method 2). Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, a dropping funnel and a nitrogen inlet, phenol (8.0g, 85.0 mmol) and potassium carbonate (13.5g, 98 mmol) were dispersed in NMP (100 mL).

Then, the mixture was heated at 150°C overnight. After the reaction mixture had been allowed to cool to 130°C, a solution of 4,4'-difluorobenzil (10.0g, 40.6 mmol) in NMP (50 mL) was slowly added through the dropping funnel. The mixture was heated at 145°C for 10h. Upon cooling down to room temperature, the mixture was filtered and the 5 filtrate was poured into 5% hydrochloric acid. The resulting precipitate was collected, air-dried, and dissolved in hot ethanol or heptane and allowed to cool to room temperature to give 13.6g (85% yield) of light yellow powder: m.p. 120-122°C. Anal. Calcd. for C₂₆H₁₈O₄: C, 79.17%; H, 4.60%. Found: C, 79.19%; H, 4.75%. FT-IR (KBr, cm⁻¹): 1666. Mass spectrum (m/e): 394 (M⁺, 100% relative abundance). ¹H NMR (DMSO-d₆, ppm) δ 7.01 -7.05 (dd, 4H, Ar), 7.05-7.10 (m, 4H, Ar), 7.19-7.26 (t, 2H, Ar), 10 7.36-7.44 (t, 4H, Ar), 7.78-7.95(dd, 4H, Ar). ¹³C NMR (DMSO-d₆, ppm) δ 117.43, 120.45, 125.06, 127.50, 130.15, 132.20, 154.83, 155.88, 162.33, 163.55.

Example 5

2,3-Bis(4-phenyloxyphenyl)-6-quinoxaline-carboxylic acid

15 Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, 3,4-diaminobenzoic acid (2.65 g, 17.4 mmol) was dissolved in acetic acid (150 mL). 4,4'-Diphenyloxybenzil (6.55 g, 16.6 mmol) was then added and heated under reflux for 12h. Upon cooling to room temperature, the resulting dark red solution was filtered and the filtrate was poured into 5% hydrochloric acid. The resulting light yellow precipitate was collected by suction filtration and air-dried. It was recrystallized from ethanol to give 7.0 g (83% yield) of bright yellow powder: m.p. 224-226°C. Anal. Calcd. for C₃₃H₂₂N₂O₄: C, 77.63%; H, 4.34%; N, 5.49%; O, 12.54%. Found: C, 77.71%; H, 4.39%; N, 5.27%; O, 12.41%. FT-IR (KBr, cm⁻¹):

1242, 1488, 1588, 1697. Mass spectrum (m/e): 510 (M^+ , 100% relative abundance). 1H NMR (DMSO-d₆, ppm) δ 6.99-7.02 (d, 4H, Ar), 7.06-7.09 (d, 4H, Ar), 7.14-7.25 (m, 2H, Ar), 7.39-7.45 (t, 4H, Ar), 7.52-7.55(d, 4H, Ar), 8.14-8.17 (d, 1H, Ar), 8.26-8.29 (dd, 1H, Ar), 8.61-8.62 (d, 1H, Ar). ^{13}C NMR (DMSO-d₆, ppm) δ 117.00, 117.66, 119.08, 119.91, 123.91, 129.01, 129.99, 130.08, 130.25, 131.57, 131.66, 131.83, 132.03, 133.13, 139.52, 142.17, 153.23, 153.83, 154.93, 155.79, 155.85, 157.55, 157.66, 160.69, 166.53.

Having thus described exemplary embodiments of the present invention, it should be noted by those skilled in the art that the disclosures herein are exemplary only and that alternatives, adaptations and modifications may be made within the scope of the present invention.